

Electroluminescence thermal quenching in SrS:Cu thin-film electroluminescent devices

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Electroluminescence (EL) thermal quenching refers a reduction in luminance, concomitant with a reduction in transferred charge, when an alternating-current thin-film electroluminescent (ACTFEL) device is operated at an elevated temperature. EL thermal quenching is found to be significant in SrS:Cu ACTFEL devices operated above ~ 60 - 80°C . Maximum transferred charge-maximum applied voltage ($Q_{\text{max}}-V_{\text{max}}$) and transferred charge capacitance (i.e., $dQ_{\text{max}}/dV_{\text{max}}$ vs V_{max}) measurements as a function of temperature in conjunction with ACTFEL device simulation are employed in order to establish that EL thermal quenching arises from a thermally activated annihilation of positive space charge and a corresponding increase in the threshold voltage.

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In the phosphor literature, thermal quenching refers to a reduction in the luminance of a phosphor when it is operated at an elevated temperature.^{1,2} Typically, thermal quenching is considered within the context of a configuration coordinate diagram and is attributed to a decreasing radiative recombination efficiency of the phosphor as the phonon density increases with increasing temperature. Thus, thermal quenching is due exclusively to an optical effect associated with the temperature dependence of the radiative recombination efficiency.

In contrast, electroluminescence (EL) thermal quenching is here employed to denote a reduction in luminance that is in excess of normal thermal quenching and is associated with a reduction in transferred charge. Thus, EL thermal quenching arises from a thermally activated electrical effect in addition to the optical effect associated with normal thermal quenching.

The purpose of this letter is to describe EL thermal quenching in SrS:Cu alternating-current thin-film electroluminescent (ACTFEL) devices, to present a model for the mechanism of thermal quenching, and to offer a method for reducing thermal quenching in this phosphor system.

The ACTFEL devices employed in this study have the standard dual insulator layer structure with aluminum and indium tin oxide top and bottom electrodes.³ ACTFEL devices fabricated by Planar (OSU) have sputtered (electron beam evaporated) phosphor layers which are rapid thermal annealed. Characterization of these devices is accomplished via temperature-dependent luminance-voltage (L-V) and maximum transferred charge-maximum applied voltage ($Q_{\text{max}}-V_{\text{max}}$) measurements.^{3,4} Note that $Q_{\text{max}}-V_{\text{max}}$ curves are often referred to as transferred charge curves.

Figures 1(a) and 1(b) show the L-V and $Q_{\text{max}}-V_{\text{max}}$ curves of a sputtered SrS:Cu ACTFEL device at 20 and 80°C . The important point to note is that the precipitous reduction in luminance at 80°C occurs concomitantly with a dramatic increase in the $Q_{\text{max}}-V_{\text{max}}$ threshold voltage. The

EL luminance at 40 V above threshold is reduced by approximately 75% in going from 20 to 80°C , whereas the photoluminescence (PL) luminance (not shown) decreases by only $\sim 20\%$ over the same temperature range. Similar EL and PL luminance reduction trends with increasing temperature are found by other researchers.⁵ Also, note in Fig. 1 that the shape of the $Q_{\text{max}}-V_{\text{max}}$ curve near threshold changes appreciably. To gain more insight into the nature of the thermally activated changes in the transferred charge curves, transferred charge capacitance curves are obtained by plotting $dQ_{\text{max}}/dV_{\text{max}}-V_{\text{max}}$,⁴ as shown in Fig. 1 (c). In addition to the increase in the threshold voltage with increasing temperature, Fig. 1 (c) shows that with increasing temperature there is a decrease in the slope of the transferred charge capacitance curve just above threshold, and a reduction and broadening of the transferred charge capacitance overshoot. Transferred charge capacitance overshoot has been ascribed to positive space charge formation in the phosphor.^{4,6-8} Thus, we attribute the decrease in the transferred charge capacitance overshoot as evidence of a thermally activated reduction in the positive space charge in the phosphor. Additionally, we propose thermally activated annihilation of positive space charge as the mechanism responsible for EL thermal quenching in SrS:Cu ACTFEL devices.

Note that EL thermal quenching is an impurity and/or defect-related property, not a fundamental property of the phosphor itself. This conclusion arises from measurements of the thermal quenching properties of SrS:Ce ACTFEL devices. Typically, the 20 to 80°C luminance at 40 V above threshold decreases by $\sim 25\%$ and the threshold voltage increases by a few volts for SrS:Ce ACTFEL devices. Thus, the properties of SrS:Ce ACTFEL devices are similar to those expected for conventional thermal quenching and are much different than the EL thermal quenching trends reported herein for SrS:Cu ACTFEL devices.

If EL thermal quenching is ascribed to thermally activated annihilation of positive space charge, the next issue is to address the nature of the positive space charge and to explain the mechanism responsible for positive space charge

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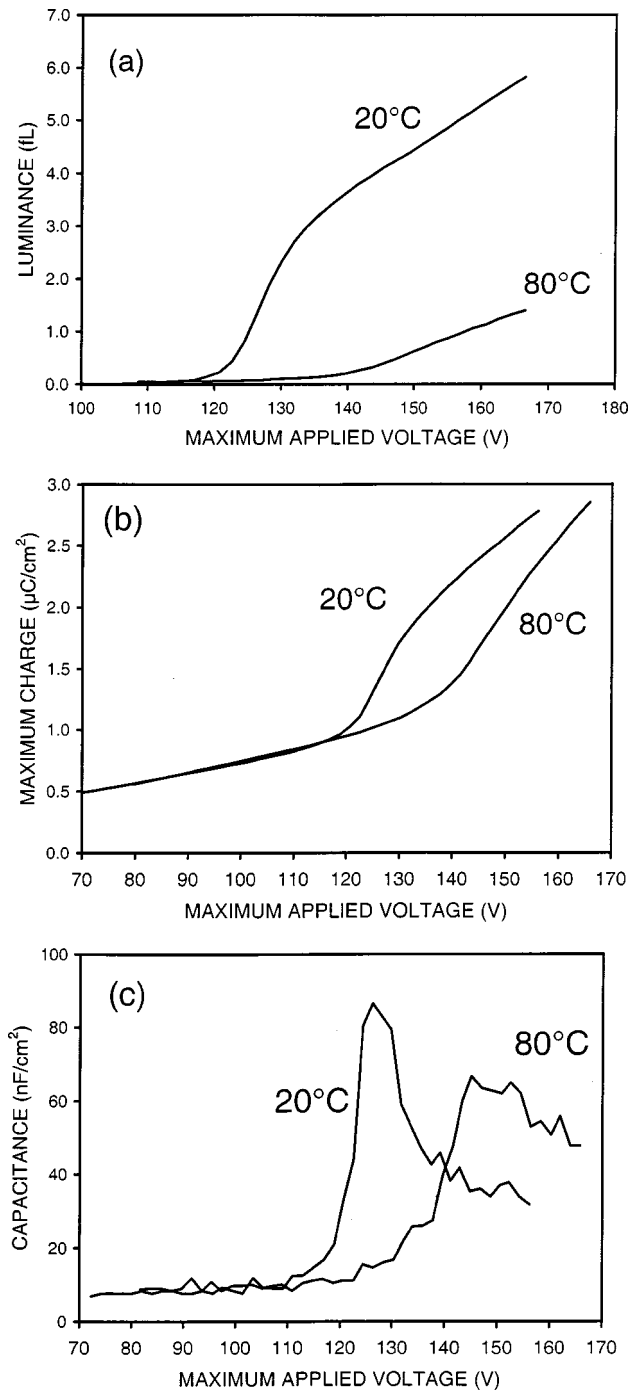


FIG. 1. (a) Luminance-voltage (L-V), (b) transferred charge ($Q_{\text{max}}-V_{\text{max}}$), and (c) transferred charge capacitance ($dQ_{\text{max}}/dV_{\text{max}}-V_{\text{max}}$) curves for a sputtered SrS:Cu ACTFEL device at 20 and 80 °C. All measurements are performed at a frequency of 60 Hz.

annihilation. There are three possible ways to create positive space charge in an ACTFEL phosphor: (i) band-to-band impact ionization and hole trapping, (ii) trap-to-band impact ionization, and (iii) electron emission from traps via thermionic emission, phonon-assisted tunneling, or pure tunneling. We believe that positive space charge creation in SrS:Cu ACTFEL devices is most likely accomplished via process (i) since simulation has shown that process (iii) does not lead to an appreciable amount of capacitance-voltage (C-V) or $dQ_{\text{max}}/dV_{\text{max}}$ overshoot.^{9,10} Additionally, we have not been able to simulate EL thermal quenching trends for process (ii); simulation shows process (ii) to be unlikely since this

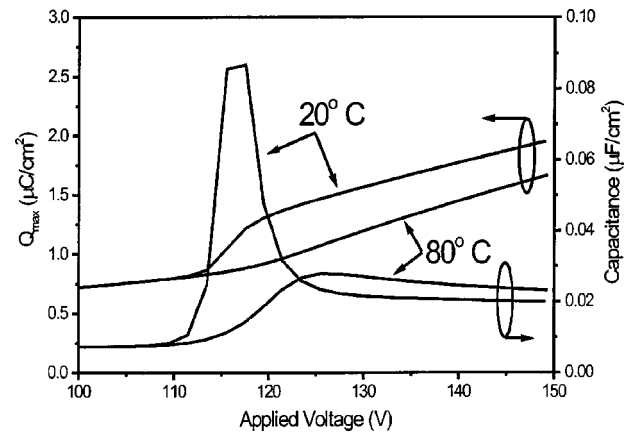


FIG. 2. Simulated transferred charge ($Q_{\text{max}}-V_{\text{max}}$) and transferred charge capacitance ($dQ_{\text{max}}/dV_{\text{max}}-V_{\text{max}}$) curves for a SrS TFEL device at 20 and 80 °C. The simulation assumes that positive space charge arises from band-to-band impact ionization and hole trapping. The hole trap density and energy depth are assumed to be $7 \times 10^{16} \text{ cm}^{-3}$ and 0.7 eV, respectively.

mechanism requires appreciable electron trap refilling to occur below threshold. Assuming process (i) is the operative positive space charge creation mechanism, an ACTFEL device physics simulation is performed¹⁰ in which the phosphor is discretized into nine sheets, each sheet is capable of trapping or emitting holes from a deep hole trap (emission is modeled as occurring via thermionic emission, phonon-assisted tunneling, or pure tunneling), holes are generated via band-to-band impact ionization, and electrons are sourced from discrete interface states.

Transferred charge capacitance simulation results are shown in Fig. 2 at temperatures of 20 and 80 °C for a hole trap density of $7 \times 10^{16} \text{ cm}^{-3}$ and energy depth of 0.7 eV. The important aspect of Fig. 2 is that the experimental EL thermal quenching trends shown in Fig. 1 (c) are consistent with the simulated trends shown in Fig. 2. In particular, with increasing temperature the threshold increases, the near-threshold slope decreases, and there is a reduction and a broadening of the transferred charge capacitance overshoot. The similarity between the measured and simulated transferred charge capacitance curves is supportive evidence for the identification of thermally activated space charge annihilation as a possible mechanism for EL thermal quenching.

Further insight into the nature of EL thermal quenching is obtained via simulation by plotting the total bulk positive space charge (i.e., the sum of all of the phosphor layer sheets) as a function of the maximum applied voltage, V_{max} , as shown in Fig. 3. This simulation reveals that, to a large extent, the threshold voltage is determined by the positive space charge formed below threshold. The prethreshold space charge concentration increases exponentially with V_{max} up to threshold. At V_{max} 's near threshold, there is a small change in the slope of the space charge density curve, corresponding to the portion of the transferred charge capacitance where overshoot is observed. Finally, at a larger V_{max} the space charge concentration saturates; this corresponds to the V_{max} above which $dQ_{\text{max}}/dV_{\text{max}}$ is equal to the insulator capacitance of the ACTFEL device. Note that the saturated space charge concentration decreases with increasing temperature; this results in an increase in threshold voltage since less positive space charge is present to aid in the injection of

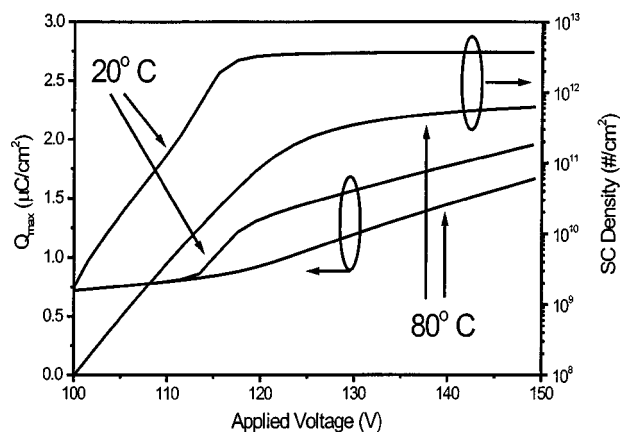


FIG. 3. Simulated transferred charge ($Q_{\max}-V_{\max}$) and total bulk positive space charge density curves for a SrS TFEL device at 20 and 80 °C. The total bulk positive space charge density is evaluated just prior to the onset of the positive applied voltage pulse. The simulation assumes that positive space charge arises from band-to-band impact ionization and hole trapping. The hole trap density and energy depth are assumed to be $7 \times 10^{16} \text{ cm}^{-3}$ and 0.7 eV, respectively.

electrons from the cathode interface. Simulation shows that this temperature-dependent decrease in the space charge concentration arises from a thermally activated flow of charge due to hole trap emission, at least for the case simulated in which the space charge creation mechanism is via process (i). If space charge creation mechanism (ii) is operative, thermally activated annihilation of positive space charge would occur via electron leakage charge and subsequent recombination in empty traps. To date, we have not been able to simulate EL thermal quenching trends if we assume that process (ii) is operative.

Transferred charge capacitance curves are also simulated (but not shown) for situations in which the hole trap concentration and energy are varied. It is found that EL thermal quenching is not eliminated by varying the hole trap concentration until the concentration becomes negligibly small. However, simulation reveals that EL thermal quenching may be eliminated if the energy depth of the hole trap is increased from 0.7 eV, as employed in Fig. 2, to 1.1 eV, even if an appreciable number of hole traps are present in the phosphor. EL thermal quenching is not observed in such a simulation since hole re-emission will not occur at an appreciable rate for a trap this deep in the temperature range of interest. Thus, one possible way to minimize or eliminate EL thermal quenching is to increase the hole trap depth, assuming that space charge creation mechanism (i) is operative.

In an attempt to minimize EL thermal quenching, we have used CuCl_2 as a dopant in SrS. Our intent is to introduce Cl donors in order to compensate Cu acceptors, thereby suppressing the formation of self-compensating sulfur vacancy donors; the hole trap energy of an isolated Cu_{Sr} acceptor is expected to be deeper than that of a Cu_{Sr} -sulfur vacancy defect complex.¹¹ Cl doping reduces the extent of EL thermal quenching somewhat, but has not eliminated it, as shown in Fig. 4. Thus, although more work is required before EL thermal quenching is eliminated in SrS:Cu ACTFEL

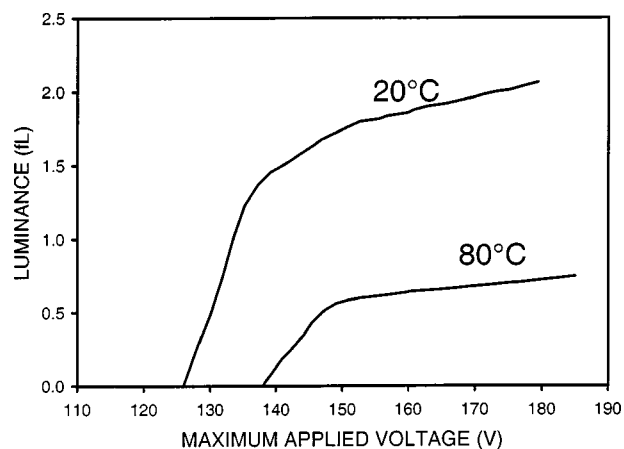


FIG. 4. Luminance-voltage (L-V) curves for an electron beam evaporated SrS:Cu,Cl ACTFEL device at 20 and 80 °C. Measurements are performed at a frequency of 60 Hz.

devices, both initial codoping experiments and simulation suggest that it may be possible to eliminate EL thermal quenching.

In summary, EL thermal quenching is used to denote a reduction in luminance in an ACTFEL device operated at an elevated temperature that is in excess of the reduction due to normal thermal quenching and occurs concomitantly with thermally induced changes in the transferred charge. EL thermal quenching is ascribed to thermally activated annihilation of space charge via the flow of excess leakage charge due to hole trap re-emission. Simulation indicates that EL thermal quenching may be eliminated if the energy depth of the hole trap associated with EL thermal quenching is shifted to a deep enough energy. Cl-codoping of SrS:Cu ACTFEL devices improves the EL thermal quenching properties of these devices, but does not lead to its elimination.

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